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(54) Title: POLYVINYLIDENE FLUORIDE MICROPOROUS MEMBRANE AND METHOD

(57) Abstract

Methods for making microporous membranes from vinylidene fluoride polymers and the products produced by these methods are described. The microporous membranes have a significantly faster flow rate at a given pore size as compared to equally-sized microporous membranes made by conventional procedures. The microporous membranes of the invention also can have significantly smaller pore sizes than conventional microporous polyvinylidene fluoride membranes. The membranes of the invention have unique macrostructural features responsible in part for their unique functional properties. The process includes dissolving the polymer in a liquid that includes a solvent and a co-solvent for the polymer. The dissolution of the polymer can be at temperatures ranging from about 20°C to about 50°C while the formation of the microporous membrane can be at temperatures ranging from about -10°C to 50°C. Selection of appropriate operating parameters of temperature and solvent/co-solvent concentration can optimize the membrane at a given nominal pore size, flow rate, and polymer distribution.

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POLYVINYLIDENE FLUORIDE MICROPOROUS
MEMBRANE AND METHOD

Field of the Invention
The invention relates to polyvinylidene fluoride microporous membranes and methods for their production. In particular, the invention relates to microporous polyvinylidene fluoride membranes that differ significantly in both their structural and functional characteristics from conventional polyvinylidene fluoride microporous membranes.

Background of the Invention
Polyvinylidene fluoride microporous membranes, generally formed as thin sheets of substantially uniform thickness, have a sponge-like internal structure containing millions of channels. These channels define a tortuous flow path for liquids from one side of the membrane sheet to the other side. Conventional methods of producing these polyvinylidene fluoride (hereinafter "PVDF") membranes result in membranes having a matrix of intercommunicating channels, the channels having a substantially uniform width within narrow limits.

Microporous membranes act as screens or sieves and retain on their surface all particles larger than the given width of a channel (i.e. pore diameter). Entrapment on the membrane surface of particles of approximately the pore diameter will rapidly plug the membrane irreversibly, leading to rapid decline in flow rate. Due to the tortuous nature of the flow channels in conventional microporous membranes, significant hydraulic pressure is needed to force liquids from one side of the membrane to the other. As the membranes clog, this pressure necessarily increases.

Conventionally-produced PVDF membranes are commercially available with average pore sizes (i.e. pore diameters) in the range from about 0.10 microns to about

5.0 microns. The smallest of these conventional pore
sizes will retain some large viruses and most bacteria.
However, most viruses and some bacteria are not retained.
In addition, the smallest of these conventional pore sizes
will not retain large macromolecules. Attempts to produce
microporous membrane filters having pore sizes less than
about 0.10 microns have generally led to problems of very
slow flow because of the small pore size, and to problems
of rapid plugging.

Conventional solvent-casting procedures for producing
microporous PVDF membranes rely on the use of a solvent
such as acetone for the PVDF polymer. Nevertheless,
acetone is usually not thought of as a solvent for this
particular polymer because it is exceedingly difficult to
dissolve any appreciable quantity of PVDF in acetone at
room temperature. In order to dissolve a sufficient
quantity to form an adequately viscous solution for use in
practicing conventional methods, the acetone must be
heated close to its boiling point of about 50°C. This
produces severe constraints on conventional methods since
the initial mixing of PVDF must occur at an elevated
temperature.

Summary of the Invention

The present invention embraces a family of microporous
PVDF membranes that substantially differ from conventional
PVDF membranes in their pore size, methanol bubble point,
flow rate, and surface area. The process for making these
unique microporous PVDF membranes includes the use of
solvents and temperatures that can be varied over a wide
range and that are chosen to permit formation of membranes
with a variety of structural and functional properties.

A microporous PVDF membrane according to one aspect of
the invention has a flow rate of solution per unit area
across the membrane that is substantially greater (i.e. at
least about 30% greater) than the flow rate of a solution
per unit area in conventional microporous PVDF membranes
of similar pore size and similar thickness. PVDF

membranes of the present invention also can have an
average pore size less than about 0.10 microns.
Particular membranes of the present invention can have
average pore sizes down to about 0.02 microns.

According to another aspect of the present invention,
there is provided microporous PVDF membranes that have a
defined microstructure which includes intercommunicating
flow channels extending from one surface of the membrane
to an opposite surface. At least one of the surfaces of
the membrane has a macrostructure. In one embodiment, the
macrostructure is defined by a plurality of substantially
spherical features having a size substantially greater
than the average pore size. In another embodiment, the
macrostructure is defined by a plurality of flattened
nodules covering substantially the entire surface of the
membrane.

In a method of the invention, a polymer is dissolved
in a mixing solution containing at least two solvents, and
the dissolved polymer then is applied to a solid substrate
as a thin film. The thin film on the substrate is
converted to a microporous membrane by displacing the
solvents from the thin film and replacing them with
nonsolvent. This occurs in a formation bath. The
formation bath is a mixture of a nonsolvent for the
polymer plus at least one of the two solvents used in the
mixing solution.

One particular aspect of the process of the invention
is the use of a solvent:co-solvent system for the polymer,
such as M-pyrrol:butylacetate or M-pyrrol:formamide. The
solvent:co-solvent system is adequate to dissolve the
polymer at temperatures between about room temperature and
about 50°C. Another aspect of the process is that
formation of the microporous membrane in the formation
bath can occur at substantially reduced temperatures. In
one embodiment of the invention, formation of the membrane
of the invention is accomplished at 0°C.

A preferred process involves forming a thin layer of a
solution of the PVDF polymer on a substrate, the PVDF

dissolved in a solvent and co-solvent. The layered
substrate is then passed into a formation bath including
at least the co-solvent plus a nonsolvent, both the
co-solvent and nonsolvent miscible with each other. The
layer of PVDF polymer is thereby transformed into a porous
membrane, formed on the substrate in the formation bath.
The membrane is removed from the substrate and then dried.

A wide variety of structural and functional properties
of the membranes can be achieved in the process by
selecting a temperature for either, or both, the mixing
solution and formation bath and also selecting a
concentration of co-solvent and nonsolvent for the
formation bath.

Description of the Drawings

Fig. 1 is a scanning electron micrograph of the top
surface of a conventional microporous PVDF membrane. The
bar represents a length of 10 microns;

Fig. 2 is a scanning electron micrograph of the top
surface of a microporous PVDF membrane of the present
invention. The bar represents a length of 10 microns;

Fig. 3 is a scanning electron micrograph of the
cross-section of the conventional PVDF microporous
membrane of Fig. 1. The bar represents a length of 10
microns;

Fig. 4 is a scanning electron micrograph of the
cross-section of the microporous PVDF membrane of Fig. 2.
The bar represents a length of 10 microns;

Fig. 5 is a scanning electron micrograph of the top
surface of another embodiment of the PVDF membrane of the
present invention. The bar represents a length of 10
microns;

Fig. 6 is a scanning electron micrograph of the bottom
surface of the conventional microporous PVDF membrane of
Fig. 1. The bar represents the length of a micron;

Fig. 7 is a scanning electron micrograph of the bottom
surface of the microporous PVDF membrane of Fig. 2. The
bar represents the length of 10 microns;

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Fig. 8 is a schematic diagram of the apparatus needed for a continuous method of the present invention.

Detailed Description of the Invention

A. Microporous PVDF Membranes

The present invention encompasses a family of microporous PVDF membranes having nominal pore sizes ranging from about 0.02 microns to about 2.0 microns. The term "nominal pore size" refers to the minimum size of particles that will be retained on the membrane. Thus, a membrane with a nominal pore size of about 0.45 microns means that particles greater than about 0.45 microns will be retained on the membrane, those less than about 0.45 microns will pass through and will not be retained.

The functional properties of these membranes differ significantly from those of conventional PVDF membranes. Specifically, the present membranes have greater liquid flow rates per unit area with equal particle retention as compared to conventionally-made PVDF membranes of the same pore size and thickness. This means that if a sample of a solution containing particles is passed through the membrane of the present invention and an equal volume sample of the same solution is passed through a conventional membrane, both membranes will retain the same amount of material, but the membrane of the present invention will have a faster flow rate and process the liquid volume in a shorter time period. Moreover, compared to conventionally-made PVDF membranes, the present PVDF membranes have an increased surface area available at the point of contact between a molecule and the surface of the membrane. This means that a sorbed molecule is more strongly held to the surface of present PVDF membranes. This is an advantage, for example, in immunodiagnostic applications where the goal is to cause small amounts of expensive molecules such as labelled reagents and tracers to be sorbed onto the surface of the membrane. These functional advantages are a direct result

of the unique structural characteristics of the membranes
of the present invention.

A scanning electron micrograph of a conventional PVDF
microporous membrane (Millipore Corporation, Bedford,
Massachusetts) of 0.22μ nominal pore size is presented
in Fig. 1. The surface morphology of this conventional
PVDF microporous membrane 10 is characterized by the
well-known features of microporous PVDF membranes; namely
a foliate (i.e. leafy), substantially flat intertwined
mesh 12 of polymeric material with a pore size determined
during manufacture. These microporous membranes have a
sponge-like matrix of intercommunicating passages
penetrating from one side of the membrane to the other
side of the membrane. These passages have a certain inner
diameter, within narrow limits. The passages are referred
to as pores 14. The pores provide a tortuous flow path
for liquids. In conventional PVDF microporous membranes,
the average width of the pores 14 as seen on the membrane
surface ranges from about 0.1 microns to about 2.0 microns
depending on the particular membrane.

Referring now to Fig. 2, the top surface of a
microporous PVDF membrane 20 of the present invention
having a substantially identical pore size (0.22μ) as
the membrane of Fig. 1 is presented for comparison.

The top surface 22 shows a much more rounded aspect
than does the conventional membrane (Fig. 1). This
microstructural morphology appears as a plurality of
globular bodies 23 attached to one another. The present
membrane also has a unique macrostructure. The term
"macrostructure" refers to morphological features of the
present PVDF membranes that have dimensions substantially
greater than the average pore size. Fig. 2 illustrates
that, in contrast to the conventional PVDF membrane of
Fig. 1, the top surface morphology of the present PVDF
membrane takes on a more cratered or pocked aspect, in
which the top surface morphology is arranged in roughly
spheroidal, cratered constructions 24 having a scale size
of the order of about 3-4 microns.

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As discussed below, microporous membranes of the present invention are formed on solid substrates in one or more solvent-containing formation baths. As used herein, the term "top surface" refers to that surface of the microporous membrane that is not engaged with the solid substrate. Conversely, the term "bottom surface" as used herein refers to that surface of the microporous membrane that is engaged with the solid substrate during formation.

Without wishing to be bound by any particular theory, it is believed that the particular macrostructural morphology of Fig. 2 is due to the orientation of the PVDF molecule as the membrane is being formed in the process of the invention. Conventional membranes, as exemplified in Fig. 1, are believed to contain fluorine atoms as part of the PVDF molecules that are not ordered in any defined manner but are randomly dispersed in several directions; thus resulting in the intertwining surface configuration of Fig. 1. In contrast, the process of the present invention is believed to orient the bulk of the fluorine atoms of the PVDF molecules toward the outer surfaces (i.e. both top and bottom) of the forming membrane. This is believed to result in the cratered appearance.

Furthermore, it is believed that the surface orientation of the PVDF molecules results in a unique configuration of the middle of the membrane, which has a lower concentration of PVDF per unit membrane as compared to the surface regions. This means that less mass of PVDF is available to be converted into a matrix of intercommunicating flow channels. Consequently, the middle portion of the membrane is believed to have a less tortuous flow path.

Fig. 3 is a vertical cross section through the same conventional microporous PVDF membrane as shown in Fig. 1. The interconnected surfaces 30 arranged parallel to the plane of the photograph are numerous, are arranged in close proximity to one another, and are densely packed in the interior of the membrane. It is believed that the

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more numerous and closer together these surfaces, the more convoluted the flow channels of the intact membrane.

In contrast, a cross-section (Fig. 4) through the same PVDF membrane as shown in surface view in Fig. 2 reveals that surfaces 40 parallel to the plane of the photograph are more globular and display the same cratered or pocked appearance as the surface morphology. This more open structure in the middle portions of the membrane is believed to be reflected as a less tortuous path of intercommunicating flow channels in the intact membrane. This results in a decrease in the physical length of a given flow channel from the top to the bottom of the membrane. The flow path a liquid travels when it traverses the present membrane is therefore much more direct than in the more tortuous channels of conventional membranes. This is believed to be the primary reason for the increased flow rate in certain of the present membranes as compared to conventional membranes of the same pore size, thickness and weight of polymer.

In addition to the altered flow path length, described above, another unique aspect of the macrostructure of the present invention is an increased surface area. This is particularly advantageous in applications requiring transfer of one or more molecules to the membrane, since there is a greatly enhanced membrane surface area at the point of contact between a molecule resting on the surface of the PVDF membrane and the membrane itself. This is believed to result from the greater amount of surface PVDF in membranes of the present invention than in conventional membranes. Because the surface area of PVDF polymer is high at the point of contact between a molecule and the membrane surface, it is believed that sorption of a molecule onto the surface of the present membrane from a target surface or another substrate will be enhanced. The increased polymer surface area available is reflected in the cratered or pocked macrostructural features, as illustrated in Fig. 2.

A second macrostructural morphology is illustrated by
the top surface 50 of a PVDF membrane (0.10μ pore size)
shown in Fig. 5. This macrostructure accounts for an
increased surface area as compared to conventional
membranes. It is produced using a particular type of
solvent, as discussed in more detail below.

Referring to Fig. 5, it can be clearly seen that the
PVDF density of the membrane surface is greater than that
in the conventional PVDF membrane of Fig. 1. The PVDF
structure shown also lacks the interconnecting
configuration as in conventional membranes and lacks the
cratered appearance of the PVDF membrane of Fig. 2. The
macrostructure illustrated in Fig. 5 is defined as being
"flat" or "flattened". The flat PVDF structure of Fig. 5
can be represented as a plurality of small globular bodies
or spheroidal nodules 52 that cover substantially the
entire surface of the membrane. These nodules can vary in
size. In the embodiment illustrated in Fig. 5, the
nodules are less than about 1 micron in diameter. Many
are on the order of tenths of microns in diameter.

Figs. 6, 7 and 8 are scanning electron micrographs of
the bottom surfaces of various PVDF membranes. In
particular, Fig. 6 is the bottom surface 60 of the
conventional microporous PVDF membrane, the same membrane
whose top surface is illustrated in Fig. 1. Both top and
bottom surfaces of this conventional membrane look
substantially the same. In contrast, Fig. 7 is a scanning
electron micrograph of the bottom surface 70 of the
microporous PVDF membrane of the present invention
previously shown in top view (Fig. 2) and vertical
cross-section (Fig. 4). The morphological features of a
cratered macrostructure 71 and globular bodies are
present. Nevertheless, these macrostructural features are
less well-developed than on the top surface (see Fig. 2).
It is believed this is due to the effect of the substrate
that is in contact with the bottom surface of the membrane
during formation.

One direct result of these unique morphological
characteristics is an increased flow rate of the present
PVDF membranes as compared to conventional membranes.
Presented below in Table I is a comparison between the
methanol bubble points and water flow rates of the present
membranes and conventional PVDF membranes (Millipore
Corp., Bedford, MA). The microporous PVDF membranes of the
present invention significantly differ with respect to
their water flow rate from conventional microporous PVDF
membranes.

The methanol bubble points (measured in pounds per
square inch above ambient atmospheric pressure) of the
present PVDF membranes are not significantly different
from the methanol bubble points of conventional PVDF
membranes even though the flow rates are higher in the
present PVDF membranes. (The term "methanol bubble point"
is a well-known check on membrane performance. The bubble
point test is based on the fact that liquid is held in the
intercommunicating flow channels of microporous membranes
by surface tension and that the minimum pressure required
to force liquid out of the channels is a measure of the
channel diameter. Briefly, a bubble point test is
performed by prewetting the membrane with methanol on one
side, applying air pressure on the other side of the
membrane and watching for air bubbles emanating from the
methanol-wetted side to indicate the passage of air
through the membrane channels. The pressure at which a
steady continuous stream of bubbles appears is the bubble
point pressure). It will be appreciated that there may be
an inverse relationship between the methanol bubble point
and the pore diameter. Thus, for a given thickness of
membrane, the higher the methanol bubble point, the
smaller the effective pore diameter. The fact that the
methanol bubble points are similar between the present
membranes of Table I and conventional membranes suggests
that the increased flow rates of the present membranes
shown in Table I may be due to the present membranes
having a greater number of flow channels of similar pore

diameter or to flow channels with less tortuous
configuration (or both) than those of conventional
membranes.

TABLE I

COMPARISON OF PREFERRED MICROPOROUS PVDF MEMBRANE WITH
CONVENTIONALLY PRODUCED MICROPOROUS PVDF MEMBRANES

	Methanol Bubble Point (psi)		Water Flow Rate (ml/min/cm^2)	
Nominal Pore Size (microns)	Present Invention	Millipore	Present Invention	Millipore
5.0	----	2-3	----	161
2.0	1.5-2	----	125-190	----
0.65	6-8	6-7	40-50	38
0.45	10-12	8-10	20-60	16
0.22	18-21	17-21	8-10	6.5
0.10	28-32	28-31	3.6-4	2.9
0.05	40-45	----	1.5-2.0	----
0.02	50-60	----	0.50-0.65	----

Referring to Table I, the microporous PVDF membranes
of the present invention: (i) encompass a wider range of
pore sizes as compared to currently available microporous
PVDF membranes; (ii) have a flow rate substantially
greater than the flow rate of conventionally-made
membranes having identical thicknesses and pore sizes; and
(iii) have a maximum flow rate (190 ml/min/cm^2) for a
2.0 nominal pore size that is not achieved even in a
conventional microporous PVDF membrane having more than
twice the pore size.

B.   The Process of Manufacture
      Conventional solvent-casting processes for making
microporous PVDF membranes generally consist of: (i)
applying a layer of a polyvinylidene fluoride polymer

dissolved in a solvent to a support surface; (ii) forming
a film of polymer on the support surface; and (iii)
passing the surface carrying the polymer film through a
formation bath containing a nonsolvent in which the
nonsolvent displaces the solvent in the film to form the
microporous membrane. The pore structure is determined by
leaching of the solvent from the film and its replacement
with the nonsolvent liquid.

In making the initial polymer solution, conventional
procedures for making PVDF membranes often required a
polymer resin to be dissolved in one solvent at an
elevated temperature (of relatively narrow range). To
provide the formation bath, a mixture of the same solvent
with a nonsolvent is provided at the same temperature as
the initial polymer solution. Moreover, in forming
microporous membranes using other kinds of polymers, it
has not been possible to use different initial dissolving
temperatures and formation bath temperatures in a way that
can predictably form a variety of microporous membrane
products.

In contrast, the process of the present invention: (i)
utilizes a range of solvent concentrations and
temperatures to predictably form porous membranes of
various pore size, polymer symmetry ratio, methanol bubble
point, and water flow rate; (ii) is not constrained to a
single solvent when using PVDF; (iii) does not require an
initial PVDF polymer dissolution at substantial one
elevated temperature; and (iv) does not require a
formation bath at the same temperature as the initial
solution.

Instead, the present method uses an initial solution
of PVDF resin in a plurality of solvents. Variation of
the operating parameters such as temperature and solvent
concentration gives precise and hitherto unknown control
over pore size, polymer symmetry ratio, flow rate, surface
morphology and thickness of the membrane.

Specifically, the temperature of the initial PVDF
mixing solution, the temperature of the formation bath in

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which the microporous membrane is formed, and/or the
relative concentration of solvents, can be selected from a
range of possible temperatures and solvent concentrations
to effect a wide range of structural and functional
changes in the PVDF microporous membrane. The temperature
of the formation bath can be substantially different than
the temperature of the initial mixing solution.
Specifically, one unique aspect of the present invention
is that the formation bath can be effectively used at
temperatures at or below the freezing point of water (0°C).

1. Solvent Systems

    Past attempts to make microporous PVDF membranes
generally involve the use of solvent materials that are
volatile and are toxic. A preferred conventional
formulation solvent used to initially dissolve PVDF
polymer is acetone. See Grandine II, U.S. Patent
4,203,848. Acetone is, however, only practical for use as
a PVDF solvent at temperatures very close to its boiling
point (50°C). At temperatures much below about 50°C, it
is difficult to get enough PVDF resin into the acetone
solution for practical purposes. Thus, conventional
methods for forming PVDF membranes require that PVDF resin
be passed into initial solution at temperatures near
50°C. This puts severe constraints on the final product
since the temperature of the initial solution, it has been
discovered, has a most significant effect on the final
pore size and other structural features of the microporous
PVDF membrane.
    One unique aspect of making the present microporous
PVDF membranes is use of solutions comprising a solvent
and preferably one or more co-solvents (i.e. a
"solvent:co-solvent system"). The term "co-solvent"
refers to organic solvents that dissolve PVDF resin slowly
at most temperatures. Because of this, by themselves,
many co-solvents are generally unsuitable for the methods
of the present invention. They are often unsuitable for
the additional reason that they tend to break down PVDF

polymer, albeit slowly, to such an extent that the PVDF
cannot reform or coagulate again in a conventional
solvent-casting process.

This property of a co-solvent, surprisingly, can be
utilized in the method of the present invention. A small
amount of co-solvent added to the solvent permits the
solvent casting procedure to be carried out over a wide
range of formation bath temperatures; even including
formation bath temperatures near zero degrees Celsius.

Co-solvents will be known to those of ordinary skill
in the art. A representative list includes formamide,
methyl isobutyl ketone, cyclohexanone, diacetone alcohol,
diisobutyl ketone, ethylacetoacetate, triethyl phosphate,
propylene carbonate, glycol ethers and glycol ether
esters. A particularly preferred co-solvent is
n-butylacetate.

The term "solvent", refers to organic compounds that
dissolve PVDF rapidly at most temperatures. This term
includes those compounds that can yield a PVDF solution of
at least 25% by weight. A preferred solvent of the
present invention is N-methyl-2-pyrrolidone (hereinafter
"N-pyrrol") although other solvents can be used, such as
dimethyl formamide, tetrahydrofuran, methyl ethyl ketone,
dimethylacetamide, tetramethyl urea, dimethyl sulfoxide
and trimethyl phosphate.

The initial dissolution of PVDF is preferably done in
a solvent:co-solvent system wherein the components are
miscible with each other. In preferred embodiments, the
solvent is about 95% N-pyrrol, the balance being one or
more selected co-solvents.

In preferred embodiments, at least about 50% of the
formation bath is a nonsolvent that is always miscible
with the other components of the bath. The term
"non-solvent" refers to organic compounds that do not
substantially dissolve PVDF at any temperature. A portion
of the same co-solvent that is in the initial PVDF
dissolution mixture also is preferably included. The
preferred nonsolvent for use in the formation bath is

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methanol. Other alkanolic nonsolvents can be used such as
ethanol and butanol provided that the nonsolvent liquid is
miscible with the other components in the formation bath.

It will be understood by those of ordinary skill in
the art that the particular aspects of the present method
including: (i) use of a solvent:co-solvent system during
initial formulation of polymer; (ii) use of the co-solvent
in the formation bath; (iii) low temperature control of
the formation bath; and other unique aspects of the
method, are not intended to be limited to use with
polyvinylidene fluoride polymers. A wide variety of
polymeric materials well-known in the art such as
polyesters, nylons, vinyl polymers, and copolymers,
polycarbonates, cellulose acetate, polysulfones and the
like that can be used in solvent-casting formation
procedures such as the ones described herein.

2.   Apparatus and Method

Apparatus and general methods for forming membranes of
the present invention are well-known to those of ordinary
skill in the art. For example, techniques for making
microporous membranes by hand are known. A polymer
solution is coated on a glass plate, which plate is then
immersed in a formation bath. After formation of the
membrane, the glass plate is dried at an elevated
temperature and the formed membrane removed from the
plate. See, U.S. Patent No. 3,642,668 (Bailey: issued
Feb. 1972). Microporous membranes described herein were
made using this manual method.

Similarly, techniques for making PVDF membranes using
a continuous process are also well-known. See for
example, U.S. Patent 4,203,848 (Grandine, II: issued May
20, 1980). A conventional apparatus and process for
continuous solvent-casting will be briefly described.

Referring to Fig. 8, equipment for production of the
present PVDF membranes includes mixing bath 42 for holding
a supply of a PVDF polymer or resin. The mixing bath
contains the substantially dry PVDF polymer, a first

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liquid that is a solvent for the polymer, and preferably,
at least one liquid that is a co-solvent for the polymer.
Both solvent and co-solvent are miscible with the
formation bath solution. In preferred embodiments of the
invention, the first liquid solvent of the mixing bath is
preferably N-pyrrol and the co-solvent is formamide and/or
N-butylacetate.

The mixing bath is provided with apparatus such as a
knife blade 44 for applying a film of the dissolved PVDF
polymer solution at a substantially uniform thickness onto
a substrate 46 that is nonporous, preferably a polyester.
The substrate is carried on a roller 47. The substrate is
driven through the remainder of the apparatus by a powered
take up roll 62.

During operation of the process, substrate 46 is
pulled through the system by takeup roll 62. As it
travels through the system, substrate 46 passes beneath
the mixing bath, which bath includes a coating blade as a
knife that is set to a predetermined gap such as, for
example, 300 micrometers. A film of polymer solution is
applied at a substantially uniform thickness onto the
substrate that travels from its supply roll to a position
underneath the knife. The film of polymer solution that
is applied to the substrate forms with that substrate a
film-substrate laminate that is caused to travel directly
into one or more formation baths.

The function of the formation bath is to convert the
film to a porous membrane. The film-substrate laminate
remains immersed in the formation bath until the pore
structure is fully formed. The laminate then travels into
extraction bath 56 where much of the solvent for the
polymer that may remain in a porous membrane is
displaced. It will be appreciated that, although Fig. 8
illustrates several formation bath tanks 50 and a single
extraction bath 56, the number of formation baths will
depend upon a variety of factors. Generally, more than
one formation bath is required in order to ensure that as
much of the solvent as possible is removed as possible

prior to separation of the formed membrane from the
substrate. Thus, the solvent displaced from the membrane
into the formation bath will gradually enrich the
formation bath. Each successive immersion in fresh
formation bath liquid will drive more of the solvent from
the membrane.

A heater (not shown) heats the solvent:co-solvent
solution in the bath 42 to elevated temperatures. A
mixer, also not shown, adds the polymer to the solution.
A separate system 52 is provided for selective heating and
cooling of formation bath liquid. Cooling the formation
bath can be performed by any one of a number of
conventional systems, preferably provided that the cooling
system can decrease the temperature of the formation bath
to at least 0°C, more preferably to about -10°C, and
increase the temperature of the formation bath to about
50°C.

The formation bath is maintained substantially in one
or more tanks 50 of generally rectangular shape. The
formation bath is a liquid that is always miscible with
the solvent and co-solvent but is a nonsolvent for the
PVDF polymer. The liquid is preferably methanol. The
remaining components of the preferred formation bath are
compatible with the mixing bath and would include
co-solvents such as formamide and N-butylacetate in
various combinations. Any solvent present in the
formation bath would be included as carry-over from the
initial mixing solution.

A roller system is provided for guiding the layered
substrate into, through, and out of the adjacent formation
baths. Multiple baths are provided so that the layered
substrate can move continuously from one bath to the
other, the nonsolvent in successive formation baths
gradually replacing the solvent and co-solvent from the
PVDF film. Such baths have associated within them a
plurality of submerged rollers 53 designed to maintain
tension of the laminate as it passes through the formation
bath. Pairs of rollers 54 are mounted adjacent to the

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formation baths and after the extraction bath 56. These
also apply tension to the layered substrate as the
substrate travels through this section. It would be
appreciated that the exact configuration of these
tensioning rollers is not critical to the operation of the
present invention.

Extraction bath 56 is positioned adjacent to the last
formation bath and is provided with a nonsolvent,
preferably water. The microporous membrane 58
spontaneously separates from the moving substrate 46 when
substantially all of the solvent has been displaced from
the membrane and the membrane matrix is fully formed.
This typically occurs in the extraction bath 56.

An extraction system 60 is positioned adjacent the
final extraction bath and receives the microporous
membrane 58. Extraction system 60 includes a drum 64
provided with a suction device 66 and spray head device
68. The membrane is disposed along an outer periphery of
drum 64 in a substantially annular channel 67 formed by
the drum and the inner surfaces of the suction 66 and
spray head devices 68. Suction device 66 engages the
membrane against the outer periphery of drum 64 and
ensures that extraction liquid is sprayed uniformly on the
membrane. The spray head 68 applies extraction liquid,
preferably water, to the membrane. The water is applied
under pressure and this helps to remove any remaining
solvent and/or co-solvent from the pores of the membrane
into the extraction system. It also removes loose
particles of polymer that are on the surface of the
membrane. This is important since any loose, surficial
particles may cause punctures in the membrane if not
removed at this stage.

After travelling through extraction bath 56, the
membrane 58 can be separated from the substrate 46.
Although Fig. 8 illustrates separation of the membrane
after passage through a plurality of formation bath tanks,
it will be appreciated that the separation of the membrane
can be achieved in a single tank depending upon the

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solvent concentration and the amount of nonsolvent
available to displace the solvent. Once separation
occurs, the used substrate 46 is passed under a tension
roll 70 and then onto a takeup roll 62. Membrane 58 is
similarly passed through a series of membrane tension
control rolls 70 to a driven windup roll 63.

Extraction system 60 provides for in-line extraction
and drying. Membrane travels over the outer surface of
drum 64. Suction is applied to the surface of the drum to
constrain the membrane against shrinkage and movement. A
series of spray heads is disposed along one arcuate
segment of the drum to apply extraction liquid to the
membrane and displace any solvent remaining in the
membrane. When suction is used, all or part of the
sprayed liquid is drawn directly through the membrane into
the drum by the applied suction and any liquid that drips
down may be caught in a separate tray (not shown).

In the final area of the drum, heat can be applied to
the membrane. This may be accomplished by heating the
drum using a device not shown such as an infrared heater,
by blowing hot air onto the membrane, or by a combination
of these and other steps. The dried membrane is then
wound on a windup roll.

The final drying stage preferably involves a heat
treatment. Such a so-called "annealing" step includes
heating the membrane above its expected temperature of use
to ensure that the membrane is dimensionally stable when
used. The operating temperatures of PVDF membranes of the
present invention range from about 0 to about 100°C.
Since the polymer has a melting point of about 160°C, a
good annealing temperature is about 130°C. The best
annealing temperature is one that is closest to the
melting point of a particular grade of PVDF without
actually melting the polymer.

The invention will now be described further by means
of several specific examples of preferred embodiments. In
the following examples, all parts and percentages are by

weight unless otherwise specified and temperatures are in
degrees Celsius.

Example 1: Production of PVDF Microporous
Membranes of Various Sizes

This example illustrates the unique versatility of the
present manufacturing process and its ability to
manufacture microporous PVDF membranes using control of
temperature and preselected solvent composition to produce
desired membrane characteristics.

The membranes were formed by hand on 6" x 8" glass
plates using conventional procedures. Briefly, an initial
solution of PVDF polymer, solvent and co-solvent were
mixed and applied to the glass plate using a coating blade
having a gap width of 15 thousands of an inch. The
coated, glass plate was immersed in a formation solution
and the membrane was allowed to form on the glass plate.
Once formed, the membranes were dried at about 50°C on the
glass plates and membrane discs were produced using a 47
mm diameter punch. The membrane thickness was measured as
well as the water flow rate $(ml/min/cm^2)$ and methanol
bubble point (psi) using standard procedures.

A.   Effect of Mixing Temperature and
Co-Solvent Composition

An initial weight of PVDF polymer (see below) was
mixed with 94-95% N-pyrrol and 5-6% N-butylacetate at
temperatures of 20°C, 35°C, 40°C, and 45°C. The formation
bath (about 20°C) contained a series of methanol
(nonsolvent) and N-pyrrol (co-solvent) or butylacetate
(co-solvent) concentrations. After the PVDF polymer was
dissolved at different initial temperatures, membranes
were formed in these different formation bath solutions.
The thickness, water flow rate, and methanol bubble point
of the membranes produced under these various conditions
was determined on the extracted and dried membranes. The
results for measurement of the water flow rate are
presented below in Table II for 375-398 gm Kynar® 761

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PVDF, (Atochem North America, Philadelphia, PA), used at different mixing solution temperatures and different solvent:co-solvent concentrations of the formation bath (20°C). Results for water flow measurement are presented in Table III for 375-398 gm Kynar® 761 PVDF used at different mixing solution temperatures and different solvent:co-solvent concentrations in the formation bath (20°C).

TABLE II

Flow Rate (ml/min/cm^2) (mean ± s.e)

Mixing Temperature (°C)	MeOH (100%)	MeOH:BA[a] (90:10)	MeOH:N-Pyrrol (90:10)
20	0.40 0.39 0.395 ± .007	0.50 0.53 0.515 ± 0.02	1.8 1.7 1.75 ± .007
35	1.9 1.6 1.75 ± 0.21	4.2 4.1 4.15 ± .007	2.1 2.5 2.3 ± .28

Thickness (mm) mean ± s.e)

20°C	160 161 160.5 ± .007	100 100 100	112 114 113 ± 1.4
35°C	100 100 100	102 105 103.5 ± 2.1	96 101 98.5 ± 3.5

Bubble Point (psi) (mean ± s.e.)

20°C	57 58 57.5 ± .70	52 51 51.5 ± .70	37 38 37.5 ± .70
35°C	36 40 38 ± 2.8	32 31 31.5 ± .70	35 37 36 ± 1.4

a.   MeOH = methanol; BA = n-butylacetate

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TABLE III

Water Flow (ml/min/cm^2)

Mixing Temp. (°C)	Methanol (100%)	MeOH:BA[a] (90:10)	MeOH:BA (80:20)	MeOH:BA (75:25)	MeOH:BA:H$_2$O (55:25:20)
20	1.6	3.2	5.0	5.4	4.3
	1.5	4.1		4.4	4.6
	1.2				
	1.1				
35	5.1	7.3	6.2	9.5	
	4.2	7.8		10.0	
	5.1	7.3		9.4	12
	4.9				
	4.3				
	4.5				
40	20		23		
			23		
			27		
45	173		173		
	161				
	156				

a. MeOH = methanol; BA = n-butylacetate

B. <u>Effect of Formation Bath Temperature</u>
<u>and Formamide</u>

A series of initial mixing solutions were made up at
40°C as follows:

<u>Solution A:</u>

Kynar®761: 400 gm
N-pyrrol: 2250 gm
n-butylacetate: 100 gm
<u>Formamide: 100 gm</u>
solids = 14% of total weight

<u>Solution B:</u>

Kynar®761: 400 gm
N-pyrrol: 2350 gm
<u>Formamide: 100 gm</u>
solids = 14% of total weight

Membranes were formed in temperature-controlled
formation baths at 0°C and 20°C. In addition, the
formation bath contained a series of decreasing methanol
concentrations and increasing formamide concentrations
(100% MeOH; 75:25 and 50:50 MeOH:Formamide). Membranes
were formed, removed from the plate, and dried as above
and their water flow rate, thickness and methanol bubble
point were measured. Results are presented in Table IV.
The dashed line indicates that a membrane did not form.
Use of formamide as a co-solvent results in formation
of a PVDF membrane having the flattened macrostructure of
Fig. 5.

TABLE IV

Water Flow (ml/min/cm²)

Formation Bath (°C)	Methanol (100%)		75% MeOH:25% Formamide		50% MeOH:50% Formamide	
	A	B	A	B	A	B
0	20	6.4	14 17	6.6	-	-
20	0.35	1.8	0.4	5.0	Membrane Collapsed	2.1

Thickness (mm)

	A	B	A	B	A	B
0	88	86	167 82	139	-	-
20	81	86	70	147	-	83

Bubble Point (psi)

	A	B	A	B	A	B
0	12	23	17 14	25	-	-
20	60	35	65	30	-	34

Initial mixing solution:

A. N-pyrrol/Butylacetate/Formamide
B. N-pyrrol/Formamide

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RESULTS AND DISCUSSION: Operating Parameters

From these data, some qualitative observations can be
made. The co-solvent composition of the formation bath
can have a profound effect on flow rate, with presence of
co-solvent slightly lowering the bubble point, but
dramatically raising the flow rate, particularly at low
formation bath temperatures (Tables II and III). This
effect of co-solvent does not extend indefinitely,
however, and if concentrations of co-solvent (especially
formamide) are much greater than about 25% by weight, the
membrane either cannot form or tends to become thinner and
more fragile (Table IV).

The temperature of the initial mixture prior to
formation appears to have a great influence on membrane
properties (Tables II and III). For any given formation
bath composition, the bubble point is lowered by
increasing the temperature of the initial mixing solution
(Table II). This results in a dramatic increase in flow
rate as the mixing solution temperature is increased from
20°C to 45°C (Table III).

Moreover, the temperature of the formation bath also
has a significant effect on the membrane properties,
particularly with co-solvents such as N-butylacetate and
formamide. As the formation bath temperature increases,
the resulting membrane shows a decreased water flow rate
and increased bubble point (Table IV). Cooling the
formation bath down to about 0°C while the membrane is
being formed results in the opposite effect; a
significantly decreased bubble point and increased flow
rate (Table IV).

Generally, a warmer mixing solution and formation bath
results in significantly increased rate of exchange of
nonsolvent for co-solvent in the pores of the forming
membrane than at lower temperatures. Further, the
dissolution of the polymer in the initial solvent is also
faster at higher temperatures. This may result in a
higher number of intercommunicating flow channels and a

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more tortuous flow path for liquid travel. This is
reflected in the higher methanol bubble point.

In the Examples, several different values were
employed for some of the more important operating
parameters. These values have been proven to produce
effective microporous membranes by many successful
demonstrations. Preferred operating ranges for some of
these parameters include a PVDF polymer concentration in
the range of between about 14% to 24% by weight of the
initial mixing solution at a preferred temperature range
of between about 20°C and about 50°C. The initial
solution preferably contains this weight of PVDF polymer
in a mixture of 95% N-pyrrol and 5% butylacetate. The
most preferred operating conditions for production of PVDF
membranes of the present invention have a co-solvent
concentration in the formation bath no greater than about
30%. The formation bath solution is made up at a
temperature in the range of -10°C to 50°C.

INDUSTRIAL APPLICABILITY

Microporous membranes of the present invention that
are produced in accordance herewith are particularly
useful in the chemical, food and pharmaceutical
industries. One particular use in forming filters with
pore sizes on the order of about 0.1 microns or less is
that the membrane may be used for removal of viruses and
large macromolecules from the fluids being processed
through the membrane. Because PVDF is chemically inert,
the membrane may be steamed sterilized repeatedly.

Another useful industrial application of the present
membranes is in tangential or cross-flow filtration
systems. In tangential or cross-flow filtration systems,
not all of the liquid volume goes through the membrane.
Some fraction of the filtrate volume can be removed and
recycled. Tangential flow systems characteristically use
tube-shaped filters or cartridges where the flow is moved
axially through the tube and material is released
transversely across the walls of the tube. Tangential

flow can be used at lower pressures than normal filtration
and the longevity of the filter is enhanced in this way.
Because the flow rates of the membranes of the present
invention are significantly faster than those of
conventional membranes of equal thickness, tangential flow
using the present membranes is particularly advantageous
because the time for processing a given volume of sample
having a given particle concentration will be much faster
than processing using conventional membranes.

Furthermore, membranes of the present invention can be
produced as a polyester supported PVDF membrane where the
polyester is encapsulated as the PVDF membrane is formed.
A particularly preferred type of PVDF membrane, however,
is a PVDF fibrous support in which the PVDF fibers are
integrally formed with the PVDF polymer as the microporous
membrane is produced.

Equivalents

It should be understood that the foregoing description
of the invention is intended merely to be illustrative
thereof, that the illustrative embodiments are presented
by way of example only, and that other modifications,
embodiments, and equivalents may be apparent to those
skilled in the art without departing from its spirit.

· Having thus described the invention, what we desire to
claim and secure by Letters Patent is:

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Claims

1.   A microporous polymeric membrane having a nominal
pore size of about 2.0 microns and a water flow rate of
between about 120-190 ml/min/cm^2.

2.   A microporous polymeric membrane having a nominal
pore size of about 0.65 microns and a water flow rate of
about 40-50 ml/min/cm^2.

3.   A microporous polymeric membrane having a nominal
pore size of about 0.45 microns and a water flow rate of
about 20-26 ml/min/cm^2.

4.   A microporous polymeric membrane having a nominal
pore size of about 0.22 microns and a water flow rate of
about 8-10 ml/min/cm^2.

5.   A microporous polymeric membrane having a nominal
pore size of about 0.10 microns and a water flow rate of
about 3.6-4 ml/min/cm^2.

6.   A microporous polymeric membrane having a nominal
pore size of about 0.05 microns and a water flow rate
between about 2.0 and 1.5 ml/min/cm^2.

7.   A microporous polymeric membrane having a nominal
pore size of about 0.02 microns and a water flow rate of
between about 0.50-0.65 ml/min/cm^2.

8.   A microporous polymeric membrane of claims 1, 2,
3, 4, 5, 6, or 7, wherein said polymer comprises
polyvinylidene fluoride.

9.   A microporous polyvinylidene fluoride membrane of
defined nominal pore size, defined thickness, and having
opposed surfaces, said membrane having a microstructure

defined by a plurality of globular bodies attached to one
another.

10. The membrane of claim 9, wherein said membrane
between said opposed surfaces has a macrostructure defined
by a plurality of spheroidal craters with an average
diameter substantially greater than the nominal pore size.

11. A microporous polyvinylidene fluoride membrane of
defined nominal pore size, defined thickness, and having
opposed surfaces, at least one of said opposed surface
having a macrostructure defined by a plurality of
spheroidal craters with an average diameter substantially
greater than the nominal pore size.

12. The membrane of claim 11, wherein said membrane
between said opposed surfaces has a macrostructure defined
by a plurality of spheroidal craters with an average
diameter substantially greater than the nominal pore size.

13. The membrane of claims 11 or 12, wherein said
membrane further comprises a microstructure defined by a
plurality of globular bodies attached to one another.

14. A microporous polyvinylidene fluoride membrane of
defined nominal pore size, defined thickness, and having
opposed surfaces, at least one of said surfaces having a
flat macrostructure defined by a plurality of spheroidal
nodules, said nodules covering substantially the entire
said surface of the membrane.

15. The membrane of claim 14, wherein, if said
nominal pore size is about 0.1 microns, then said
spheroidal nodules have an average diameter less than
about 1 micron.

16. In a method of making a microporous
polyvinylidene fluoride membrane of a defined nominal
pore size, comprising;

dissolving the polyvinylidene fluoride polymer in a
mixing solution containing a solvent at a first
temperature;

disposing the solution onto a substrate as a thin
film;

immersing the substrate and thin film in a formation
bath at a second temperature, said formation bath
containing a nonsolvent for the polymer; and converting
the dissolved polymer thin film disposed on the substrate
in the nonsolvent-containing formation bath into a
microporous membrane, wherein the improvement comprises:

dissolving the polymer in a mixing solution containing
a co-solvent for the polymer, as well as the solvent.

17. The method of claim 16, wherein the solvent
comprises N-pyrrol and the co-solvent is seleted from the
group consisting of butylacetate and formamide.

18. The method of claim 17, further comprising
selecting at least the first temperature and selecting at
least the second temperature to optimize the membrane at a
given nominal pore size.

19. The method of claim 18, wherein the step of
selecting the second temperature includes selecting a
temperature within the range from about -10°C to about
50°C.

20. The method of claim 16, further comprising
selecting at least the nonsolvent and co-solvent
concentration for said formation bath to optimize the
membrane at a given nomimal pore size.

21. The method of claim 16, further comprising selecting at least the first temperature and at least the second temperature to optimize the membrane at a given polymer symmetry ratio.

22. The method of claim 16, further comprising selecting at least the nonsolvent and co-solvent concentration for said formation bath to optimize the membrane at a given polymer symmetry ratio.

23. A process for making a microporous membrane from polyvinylidene fluoride, comprising:
    forming a thin layer of a solution of the polyvinylidene fluoride on a substrate, the polyvinylidene fluoride dissolved in a plurality of solvents;
    passing the substrate into a formation bath comprising at least one solvent for the polymer and a nonsolvent for the polymer, the nonsolvent being miscible with said at least one solvent for the polymer;
    forming a porous membrane on the substrate;
    removing at least one solvent and the nonsolvent from the porous membrane;
    separting the membrane from the substrate; and
    drying the porous membrane,
    wherein the plurality of solvents for the polyvinylidene fluoride comprises a solvent and a co-solvent, and further wherein said formation bath includes at least said co-solvent.

24. The process of claim 23, wherein the step of passing the substrate into a formation bath, comprises passing the substrate into a formation bath containing a co-solvent selected from the group consisting of n-butylacetate, formamide and combinations thereof.

25. A continuous process for forming a microporous membrane from a polymer that is at least about 14% by

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weight of polyvinylidene fluoride, comprising the steps of:

applying a layer of a solution comprising the polymer
in a solvent:co-solvent system at a certain polymer
concentration as a thin layer to a surface of a traveling
substrate;

immersing the substrate carrying the layer of polymer
solution in a formation bath liquid comprising a mixture
of methanol and at least the co-solvent, the co-solvent
forming from about 0% to about 50% of the bath, and the
balance being methanol;

maintaining the layer immersed in the formation bath
by passing it through said formation bath to permit
replacement of any solvent and co-solvent in the layer
with the formation bath liquid, until the layer has been
converted to a microporous polyvinylidene fluoride
membrane having an average pore size from about 0.02
microns to about 2 microns, wherein the pores
intercommunicate and are of substantially uniform size;

separating the formed polyvinylidene fluoride membrane
from the substrate;

washing the polyvinylidene fluoride membrane with
water to extract any residual solvent, co-solvent or
formation bath liquid from the membrane and then;

drying the membrane to remove water.

26.   The process of claim 25, wherein the layer of
polymer solution is applied at a temperature ranging from
about 20°C to about 55°C.

27.   The process of claim 25, wherein the step of
maintaining the layer immersed in the formation bath
comprises selecting a formation bath temperature ranging
from about -10°C to about 50°C.

28.   The process of claim 25, wherein the polymer
concentration in the polymer solution is in the range from
about 14% to about 24% by weight of the solution, and

wherein the nonsolvent concentration in the formation bath is from about 50% to about 100% by weight of the bath, and the concentration of co-solvent in the formation bath is from about 0% to about 50% by weight of the bath.

29. A composition for forming a microporous polymer membrane, comprising a polymer in combination with at least one compound selected from the group consisting of N-pyrrol, methanol, butylacetate, and formamide.

30. The composition of claim 29, wherein said polymer is polyvinylidene fluoride.

31. The composition of claim 30, wherein said polyvinylidene fluoride comprises between about 14% to about 24% by weight.

32. The composition of claim 29, wherein said at least one compound comprises N-pyrrol combined with butylacetate.

33. The composition of claim 29, wherein said at least one compound comprises methanol combined with butylacetate.

34. The composition of claim 29, wherein said at least one compound comprises methanol combined with formamide.

35. The composition of claims 33 or 34, wherein said methanol comprises between about 50% and about 100% by weight.

36. The composition of claim 34, wherein said formamide comprises between about 30% to about 10% by weight.

37. The composition of claim 33, wherein said
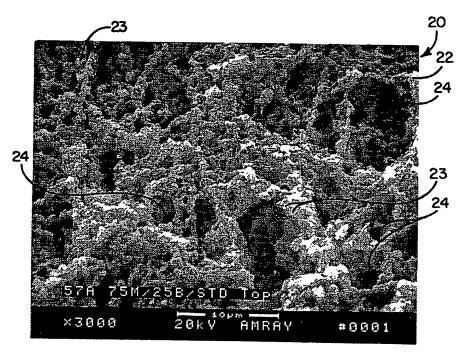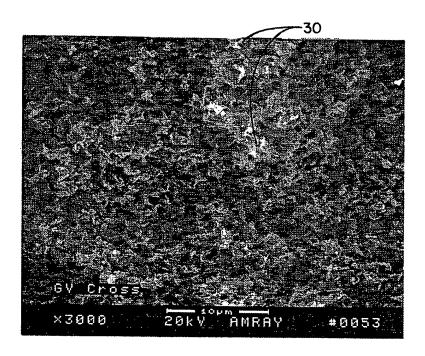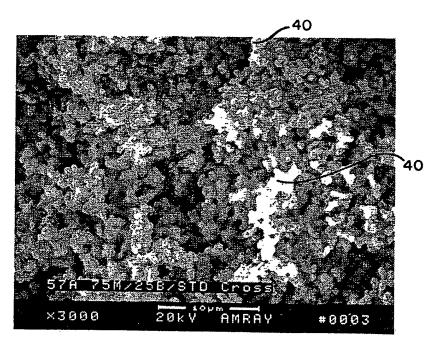butylacetate comprises between about 30% to about 10% by
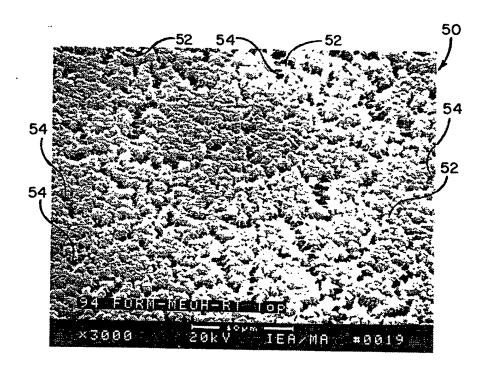weight.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

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Fig. 6
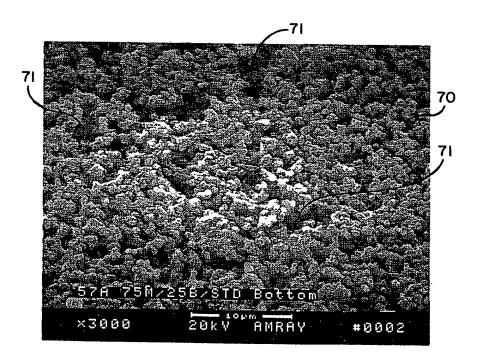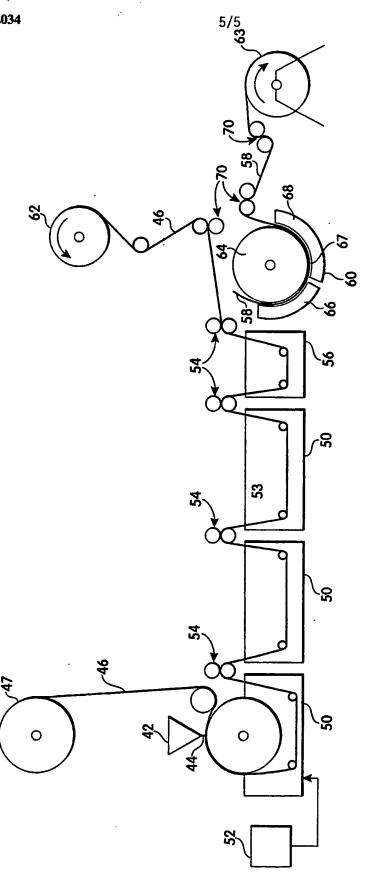

Fig. 7

Fig. 8

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]
According to International Patent Classification (IPC) or to both National Classification and IPC
Int.Cl. 5 B01D61/02; B01D71/34

II. FIELDS SEARCHED	
Minimum Documentation Searched[7]	
Classification System	Classification Symbols
Int.Cl. 5	B01D
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]	

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category°	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	WO,A,9 117 204 (MEMTEC LTD.) 14 November 1991 see page 27 ---	1,16
A	EP,A,0 111 663 (GAMBRO, INC. ET AL.) 27 June 1984 ---	1
A	DATABASE WPI Week 8903, Derwent Publications Ltd., London, GB; AN 89020416 & JP,A,63 296 940 (TORAY IND INC) 5 December 1988 see abstract ---	16,17
A	DE,A,2 632 185 (SUMITOMO ELECTRIC INDUSTRIES, LTD.) 27 January 1977 ---	16
	-/--	

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION	
Date of the Actual Completion of the International Search 05 AUGUST 1993	Date of Mailing of this International Search Report 2 6. 08. 93
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer DEVISME F.R.

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category°	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 16, no. 338 (C-965)22 July 1992 & JP,A,41 00 522 (NOK CORP) 2 April 1992 see abstract ---	16
A	US,A,4 946 889 (AKINORI NISHIOKA) 7 August 1990 -----	17

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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		JP-A-	59103671	15-06-84
		SE-A-	8206515	17-05-84
		US-A-	4935140	19-06-90
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		JP-B-	53015949	29-05-78
		CA-A-	1068458	24-12-79
		FR-A,B	2333825	01-07-77
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